THE STANDARD CHEMICAL OXYGEN-IODINE
LASER KINETICS PACKAGE

Revised 27 Apr 89

Capt G. P. Perram
Dr G. D. Hager

October 1988

Final Report

Approved for public release; distribution unlimited.

DTIC
ELECTE
MAY 3 1 1989
S D

AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
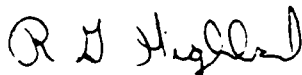Kirtland Air Force Base, NM 87117-6008

89 5 31 001

89 1 05 108

This final report was prepared by the Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico, Job Order 33261U01. Dr R. G. Highland, (AFWL/ARBI) was the Laboratory Project Officer-in-Charge.

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely Government-related procurement the United States Government incurs no responsibility nor any obligation whatsoever. The fact that the Government may have formulated or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise in any manner construed, as licensing the holder or any other person or corporation; or as conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been authored by an employee of the United States Government. Accordingly, the United States Government retains a nonexclusive, royalty-free license to publish or reproduce the material contained herein, or allow others to do so, for the United States Government purposes.
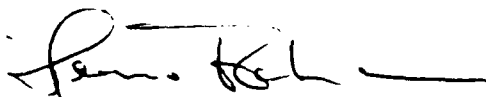
If your address has changed, if you wish to be removed from our mailing list, or if your organization no longer employs the addressee, please notify AFWL/ARBI, Kirtland AFB, NM 87117-6008 to help us maintain a current mailing list.

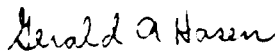This report has been reviewed and is approved for publication.

R. G. HIGHLAND, PHd
Project Officer

FOR THE COMMANDER

GERALD A. HASEN
Lt Col, USAF
Chief, Advanced Chemical Laser Br

HARRO ACKERMANN
Lt Col, USAF
Chief, Laser Science Technology Off

AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base
New Mexico 87117-6008

27 April 1989
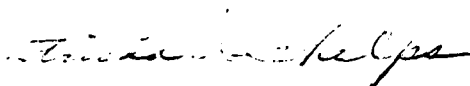
ERRATA

AFWL-TR-88-50   THE STANDARD CHEMICAL OXYGEN-IODINE LASER KINETICS
PACKAGE

Please replace new pages in your document.

    Page 7
    Page 8
    Page 9
    Page 10
    Page 11
    Page 16
    page 18
    Page 20
    Page 21
    Page 22

Authority:
Glen P. Perram
Captain, USAF
Chief, Visible Chemical Laser Section

[signature]

PATRICIA J. PHELPS
Chief, Technical Reports Branch

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
	Approved for public release;
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFWL-TR-88-50	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Air Force Weapons Laboratory		

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Kirtland Air Force Base, New Mexico 87117-6008	

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO
	62601F	3326	1U	01

11. TITLE (Include Security Classification)

THE STANDARD CHEMICAL OXYGEN-IODINE LASER KINETICS PACKAGE

12. PERSONAL AUTHOR(S)
Perram, Glen P. and Hager, Gordon D.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 08/87 TO 03/88	1988, October	36

16. SUPPLEMENTARY NOTATION   Supersedes AD-A202 223

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Chemical Oxygen-Iodine Laser
09	03		Kinetics
			Chemical Laser

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This report presents the Air Force Weapons Laboratory Standard Chemical Oxygen-Iodine Laser Kinetics Package. A complete reaction scheme including recommended rate coefficients for modeling the gas phase kinetics of chemical oxygen-iodine lasers (COIL) was established to provide a common basis for the research and development of COIL devices. A review of the experimental kinetic data base from which this model was derived is also presented. However, the fully coupled, reactive mixing and optical physics problems inherent in supersonic chemical oxygen-iodine lasers are not addressed.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Dr R. G. Highland	(505) 844-0661	ARBI

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   All other editions are obsolete.
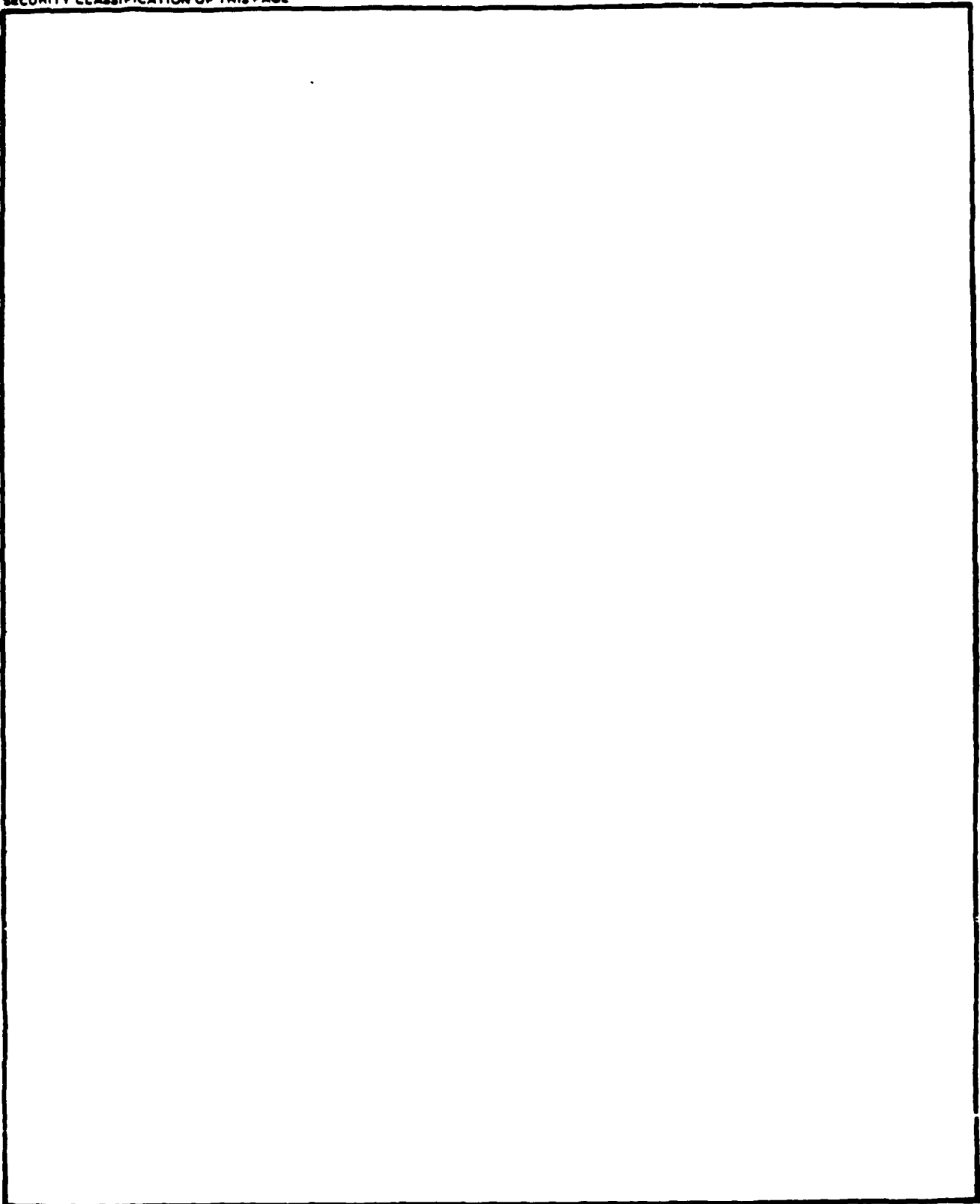
PREFACE

This technical report presents the edited proceedings from the Air Force
Weapons Laboratory Conference on Chemical Oxygen-Iodine Laser Kinetics held on
11 August 1987 at R&D Associates, 2301 Yale Blvd SE, Albuquerque, New Mexico.
An expert panel was convened to review the data base and to recommend a stan-
dard package for the gas phase kinetics pertaining to chemical oxygen-iodine
lasers. The members of this panel were:

Chairman	Conference Organizer
Dr R. F. Heidner Aerospace Corporation	Dr D. N. Plummer R&D Associates
Dr H. V. Lilenfeld McDonnel Douglas Research Laboratories	Dr P. L. Houston Cornell University
Dr R. F. Shea Los Alamos National Laboratory	Dr S. J. Davis Physical Sciences Inc
Dr C. W. Clendening TRW Space & Technology Group	Dr J. Blauer Rockwell International
Dr W. Warren Pacific Applied Research	Dr D. J. Benard Rockwell Science Center

A complete documentation of this conference entitled "Proceedings of the 1987
Air Force Weapons Laboratory Conference on Chemical Oxygen-Iodine Laser
Kinetics" was prepared by R&D Associates, the Aerospace Corporation, and the
Air Force Weapons Laboratory and may be obtained from:

R&D Associates   or   Advanced Chemical Laser Branch
Systems Engineering Division   Air Force Weapons Laboratory
P.O. Box 9377   Kirtland AFB, NM 87117-6008
Albuquerque, NM 87119
(505) 243-5609   (505) 846-0519

The editors of this report would like to acknowledge the major contributions
by R. F. Heidner and D. N. Plummer to the preparation of the conference pro-
ceedings and by the panel members through their presentations and discussions.

CONTENTS

FIGURES

TABLES

1.0 INTRODUCTION

The Chemical Oxygen-Iodine Laser (COIL) is the shortest wavelength high energy chemical laser in existence today and has great potential for Air Force directed energy weapons applications. The Air Force Weapons Laboratory (AFWL), Kirtland Air Force Base, New Mexico, is vigorously pursuing the development of efficient, scalable COIL devices with high output power and excellent beam quality. While chemical oxygen-iodine lasers are in the early stages of large scale development, a 25 kW device is being built at AFWL and scaling to larger devices is currently under active investigation.

It has been long recognized that continuous-wave (CW) chemical lasers represent an extremely complex interaction between fluid mechanics, chemical kinetics, and optical physics. It is truly impossible to focus on one area without acknowledging its interdependence with the others. The chemical oxygen-iodine laser presents additional problems in that the energy storage medium, singlet oxygen, is generated by a liquid-gas phase reaction. The kinetics of chemical oxygen-iodine lasers can be divided into five categories: (1) the chemistry of singlet oxygen generators, (2) the chemistry of COIL in the presence of water aerosols, (3) transport of singlet oxygen in the absence of iodine, (4) the dissociation of molecular iodine by excited oxygen, and (5) the kinetics of iodine atoms and excited oxygen. Only the last three kinetics topics are covered in this review.

A large variety of research and engineering groups are involved in the development of COIL technology. A standardization of the chemical kinetics for COIL device modeling and data interpretation, gas phase kinetics studies, and power scaling studies is required to allow for optimal information exchange. A conference on chemical oxygen-iodine laser kinetics was held by R & D Associates for AFWL on 11 August 1987 and this report summarizes the proceedings of this meeting. Specifically, the AFWL Standard Chemical Oxygen-Iodine Laser Kinetics Package is developed and reported.

Several reviews of the gas phase kinetics of COIL devices are available in the literature (Refs. 1--4). The previous AFWL standard COIL rate package was compiled by R.F. Shea (Ref. 5) in an informal document (16 November 1982) with addenda relating to optical broadening coefficients for iodine atoms

(15 November 1982) and iodine dissociation kinetics (12 November 1982). The current AFWL rate package is a revision of that document based on research in the intervening five years and on the deliberations of the current panel.

The purpose of the AFWL Standard Chemical Oxygen-Iodine Laser Kinetics Package is to provide a baseline modeling condition to compare the predictions, analyses, and results of diverse research groups. It is not intended to stifle more novel and comprehensive modeling efforts. Indeed, the Air Force encourages continued consideration of the many, complex issues associated with modeling the performance of COIL devices. However, AFWL does request that such research efforts always be compared to the baseline model presented in this document.

An important philosophical aspect of this standard rate package is simplicity. The package was designed to include the important kinetic processes involved with small scale flow tube experiments as well as high power oxygen-iodine lasers, while at the same time being simple enough to allow for economic application and direct interpretation. The model includes only information that is directly supported by experimental evidence. This package addresses only the gas phase kinetics of COIL and specifically excludes any discussion of the fully coupled chemical kinetics, fluid mechanics and optical physics problems.

2.0 OVERVIEW OF THE CHEMICAL OXYGEN-IODINE LASER

The chemical oxygen-iodine laser, which operates on the hyperfine components of the $5^2P_{1/2} \longrightarrow 5^2P_{3/2}$ transition in atomic iodine, is chemically pumped through energy transfer from the metastable energy carrier, $O_2(^1\Delta)$. The energy levels for molecular iodine and oxygen and atomic iodine are shown in Fig. 1. The singlet oxygen is produced by a two phase reaction of chlorine gas and liquid basic hydrogen peroxide (Ref. 6). Molecular iodine is injected into the primary oxygen flow and is dissociated to atomic iodine by way of a complicated, multistep reaction mechanism (Ref. 7). Once iodine atoms are produced, an equilibrium between excited iodine atoms and singlet oxygen is rapidly attained through the nearly resonant energy transfer reactions given by $I(^2P_{3/2}) + O_2(^1\Delta) \rightleftharpoons I(^2P_{1/2}) + O_2(^3\Sigma)$. A condition for zero gain at T = 295 K is achieved when the ratio of $O_2(^1\Delta)$ to total oxygen is approximately 0.17 (Ref. 8). Continuous-wave lasing action is achieved on a single hyperfine transition of the inhomogeneously broadened iodine atom at 1.315 μm.

Subsonic and supersonic COIL devices have been demonstrated based on this reaction scheme. The performance of these lasers indicates great potential for scaling to higher powers. The description of the gas phase kinetics of these devices is incomplete, however.
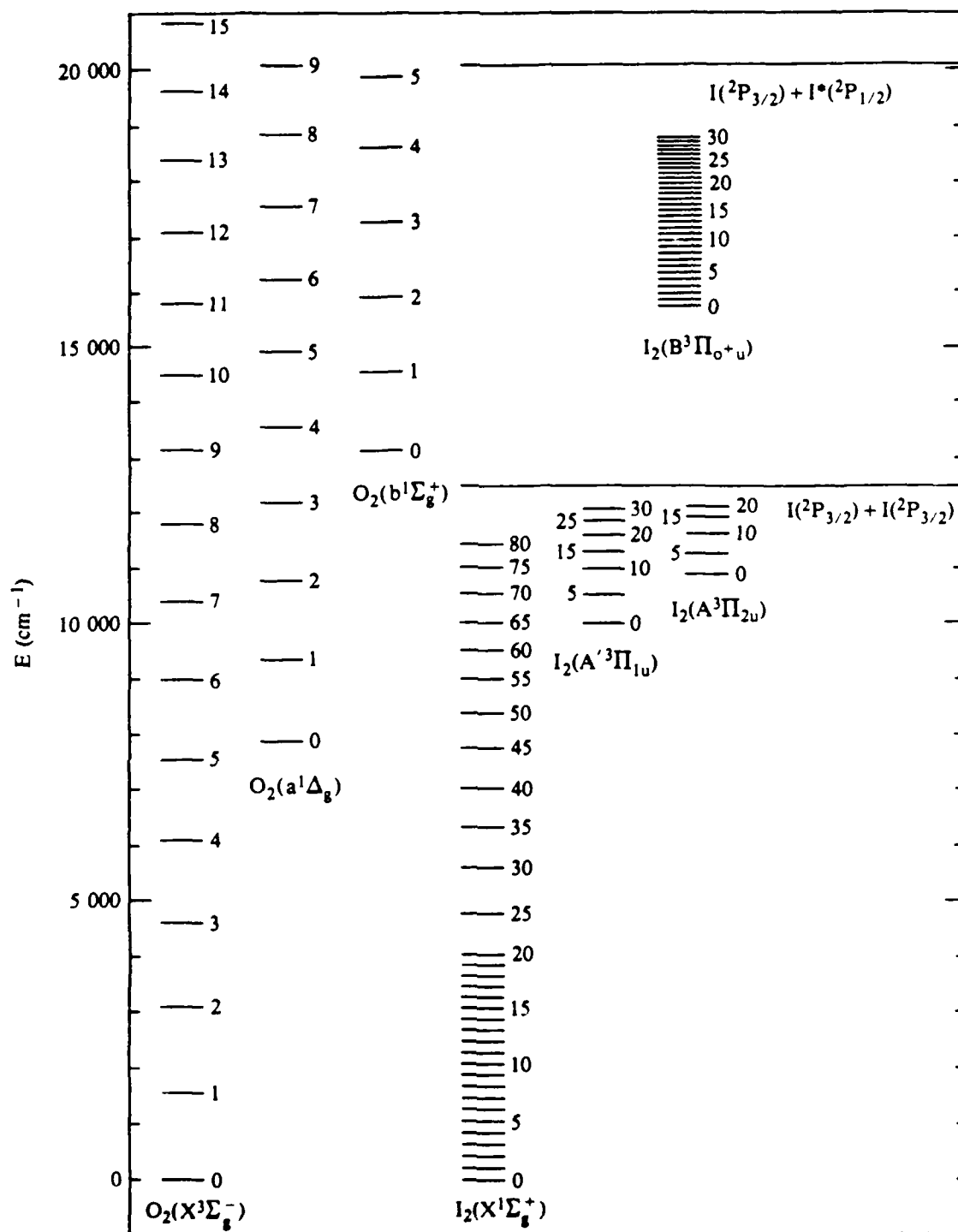
Figure 1. Energy level diagram for the oxygen-iodine system. Electronic and vibrational states for I_2, O_2, and I are shown on the same scale. This figure is reproduced from Ref. 20.

3.0 REVIEW OF THE KINETIC DATABASE

An overview of the chemistry involved with supersonic COIL devices is shown in Fig. 2. The generation of singlet oxygen is a separate topic and will be reviewed in a subsequent report. The following paragraphs will review the current understanding of: (1) the transport of oxygen to the iodine nozzle assembly, (2) the dissociation of molecular iodine by excited oxygen, and (3) the free iodine atom laser cavity kinetics. The chemistry and physics of water aerosols is an important aspect of COIL device modeling, but will not be discussed in this report.

3.1 SINGLET OXYGEN TRANSPORT

The gas phase kinetics of $O_2(a^1\Delta)$ and $O_2(b^1\Sigma)$ are quite well understood. These states are well isolated from the other electronic states of oxygen which have energies greater than 3 eV. The radiative lifetime of $O_2(^1\Delta)$ is 45 min (Ref. 9) and the energy pooling of $O_2(^1\Delta)$ to produce $O_2(^1\Sigma)$ is slow (Ref. 10) which allows for the transport of singlet oxygen to the iodine nozzle with low loss. Table 1 gives the recommended rate coefficients for the deactivation of singlet oxygen in the absence of iodine. The Tables 1--4 present the kinetic data base and give a single best value for each rate coefficient from the literature, rather than a weighted mean. All rate coefficients cited in this report are labeled according to the process number scheme listed in Tables 1--4. A confidence level of high (H), medium (M) or low (L) is suggested. In addition, an indication of the importance of the reaction to the complete mechanism is assigned for each process.

The crucial issues in the transport of singlet oxygen are the energy pooling rate, k_1, and the total second order $O_2(^1\Delta)$ removal rate, $k_1 + k_2 + k_3$. Three absolute measurements of k_1 (Refs. 10, 11 & 12) and three measurements of the temperature dependence for $k_1(T)$ (Refs. 10 & 13) have been reported. The rate coefficient measured by H. V. Lilenfeld (Ref. 10) is preferred because the $O_2(^1\Delta)$ concentration is measured by an EPR technique. The agreement among all measurements is good.

Evaluating the second-order loss of $O_2(^1\Delta)$ is somewhat more difficult, but extremely important. The rate for total second order removal of $O_2(^1\Delta)$ is
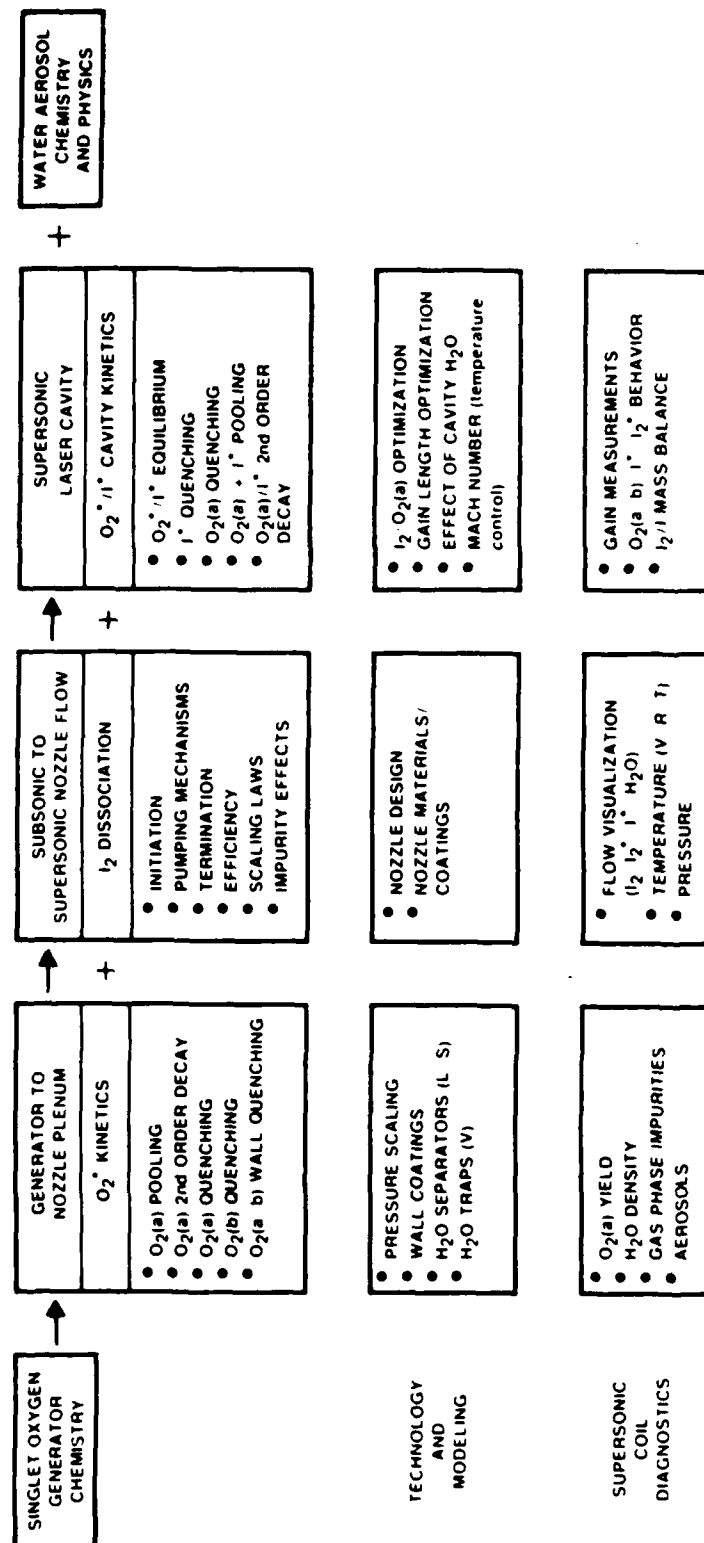
Figure 2. Overview of COIL chemistry modeling showing five distinct kinetics topics.

TABLE 1. O_2^* Kinetics: Generator to nozzle plenum.

Kinetic Process	Recommended Rate Coefficient (cm³/molecule-s)	Confidence Level	Importance to Model	Reference
1. O21D + O21D → O21S + O21S	$(2.7 \pm 0.5) \times 10^{-17}$	H	H	10
2. O21D + O21D → O21D + O21S	0	L	H	10
3. O21D + O21D → O21S + O21S	$(1.7 + 1 -.5) \times 10^{-17}$	L	H	10
4. O21S + O21S → O21D + O21S	$(3.9 \pm 0.2) \times 10^{-17}$	H	L	16
5. O21S + H2O → O21D + H2O	$(6.7 \pm 0.5) \times 10^{-12}$	H	H	17
6. O21S + Cl2 → O21D + Cl2	$<2 \times 10^{-15}$	M	L	18
7. O21S + H2O2 → O21D + H2O2	3.3×10^{-13}	L	M	19
8. O21S + He → O21D + He	1×10^{-17}	L	L	20
9. --	--	-	-	--
10. Reserved for model expansion				--
11. O21S (+ wall) → O21D (+ wall)	$(\gamma = 10^{-2})$ Glass; $(\gamma = 10^{-3})$ Heliocar.	M; M	L; L	Numerous; Numerous
12. --	--	-	-	--
13. Reserved for model expansion				--
14. O21D + O21S → O21S + O21S	$(1.6 \pm 0.05) \times 10^{-18}$	H	H	21
15. O21D + H2O → O21S + H2O	$(4 \pm 1) \times 10^{-18}$	M	M	20
16. O21D + Cl2 → O21S + Cl2	$(6 \pm 3) \times 10^{-18}$	M	M	22
17. O21D + H2O2 → O21S + H2O2	--	L	L	--
18. O21D + He → O21S + He	$(8.0 \pm 2.6) \times 10^{-21}$	H	L	23
19. Reserved for model expansion	--	-	-	--
20. O21D (+ wall) → O21S (+ wall)	$[\gamma = (2 \pm 1) \times 10^{-5}]$ Glass	M	H	Numerous

TABLE 2. I_2 dissociation by O_2^*

Kinetic Process		Recommended Rate Coefficient $(cm^3/molecule-s)$	Confidence Level	Importance to Model	Reference
21. I2X + O2IS	→ I + I + O2IS	$<4 \times 10^{-12}$	M	H	24
22. I2X + O2IS	→ I2X + O2ID				
23. I2X + O2IS	→ I2X + O2IS	1.6×10^{-11} (a)	L	H	17
24. I2X + O2IS	→ I2A1A2 + O2IS				
25. I2A1A2 + O2ID	→ I + I + O2IS	$>1 \; 10^{-11}$	M	M	25
26. I2A1A2 + O2ID	→ I2B + O2IS	--	-	-	--
27. I2A1	→ I2X + hv	$3.8 \times 10^3 \; (s^{-1})$	M	M	25
28. I2A1 + M	→ I + I + M	--	L	H	--
29. I2A2 + M	→ I + I + M	2.4×10^{-12} (SF$_6$) 5.5×10^{-11} (I2) 2.6×10^{-14} (Ar) 3.5×10^{-14} (N2) 0.94×10^{-14} (He)	L	M	--
30. I2B	→ I + I	$(10^6 \; s^{-1})$	H	L	26
31. I2B	→ I2X + hv	$(5 \times 10^5 \; s^{-1})$	H	L	26
32. I2X + O2ID	→ I2* + O2IS	7×10^{-15}	L	M	27
33. I2X + I*	→ I2* + I	$(3.8 \pm 0.3) \times 10^{-11}$ (b)	M	H	28
34. I2* + O2ID	→ I + I + O2IS	3×10^{-10}	L,M	H	27
35. I2* + O2IS	→ I2X + O2IS	5×10^{-11}	L,M	H	27
36. I2* + H2O	→ I2X + H2O	3×10^{-10}	L,M	H	27

(a) This rate coefficient is for all product channels other than (21), i.e. (22)-(24)

(b) The measured rate coefficient is for I* disappearance. The rate of I_2^* production is assumed.

8

TABLE 3. Cavity kinetics (fully dissociated I_2).

Kinetic Process		Recommended Rate Coefficient $(cm^3/molecule\text{-}s)$	Confidence Level	Importance to Model	Reference
37. I_2^* + He	→ I_2X + He	4×10^{-12}	L	M	Assume same as Ar
38. I_2^* + Ar	→ I_2X + Ar	4×10^{-12}	L,M	M	27
39. I_2^* (+ wall)	→ I_2X (+ wall)	$(3 \times 10^3\ s^{-1})$	L,M	L,M	10
40. I + O2ID	→ I^* + O2S	$(7.8 \pm 0.8) \times 10^{-11}$	H	M	10
41. I^* + O2S	→ I + O2ID	$(2.7 \pm 0.3) \times 10^{-11}$	H	M	29
42. I + O2ID	→ I + O2S	$<1 \times 10^{-15}$	M	L	8
43. I^* + O2S	→ I + O2S	$<3.5 \times 10^{-16}$	M	L,M	8
44. I^* + O2ID	→ I + O2IS	1.0×10^{-13}	H	M	10, 13
45. I^* + O2ID	→ I + O2ID	1.1×10^{-13}	M	M	8
46. I^* + O2ID	→ I + O2S	0	M	M	8
47. I^* + I	→ I + I	$<1.7 \times 10^{-13}$	M	L	8
48. I^* + H2O	→ I + H2O	$(2.1 \pm 0.3) \times 10^{-12}$	H	M	30
49. I^* + H2O2	→ I + H2O2	$(2.5 \pm 1.5) \times 10^{-11}$	L	M,H	31, 32
50. I^* + He	→ I + He	$<5 \times 10^{-18}$	L	L	33
51. Reserved for model expansion		--	--	--	--
52. I^* + wall	→ I + wall	$\gamma < 10^{-3}$ (Halocarbon)	L	L	8
53. I^*	→ I + hv	$7.8\ sec^{-1}$	H	L	34

9

TABLE 4. Supplementary kinetics processes.

Kinetic Process		Recommended Rate Coefficient (cm³/molecule-s)	Confidence Level	Importance to Model	Reference
A. Chlorine Catalytic Cycle					
54. I* + Cl2	ICl + Cl	$(5.5 \pm 0.8) \times 10^{-15}$	M	L	25
55. I* + Cl2	I + Cl$_2$	$< 8 \times 10^{-15}$	M	M	35
56. I* + ICl	I2X + Cl	1.5×10^{-11}	M	L	25
57. I2X + Cl	ICl + I	2×10^{-10}	L	L	27
58. ICl + Cl	Cl2 + I	$(8 \pm 1 \times 10^{-12})$	M	L	36
B. I Atom Recombination					
59. I + I + I2X	I2X + I2X	3.6×10^{-30} (cm⁶/s²)	H	L,M	
60. I* + I + I2X	I2B + I2X	$<<3.6 \times 10^{-30}$ (cm⁶/s⁶)	L	L	
61. I*(I) + Wall	1/2I2X	(Y = 2.5×10^{-4}), (Halocarbon) Y $\leq$ 1 (metals)	M / L	L / M	8,11

$6 \pm 2 \times 10^{-17}$ cm^3/molecule-s (Ref. 10). On comparison of this result with the measured value for k_1, two interpretations of this rate can be made (Ref. 14); $O_2(^1\Delta)$ could pool to $O_2(^1\Sigma)$ followed by $O_2(^1\Sigma)$ quenching to ground state oxygen, $O_2(^3\Sigma)$. Such an interpretation requires $k_2 + k_3 = 0$. A more widely accepted view is that $O_2(^1\Sigma)$ is quenched to $O_2(^1\Delta)$ which requires $k_2 + 2k_3 = 3 \times 10^{-17}$ cm^3/molecule-s. No further deconvolution is possible. Note that one must be very careful not to mix these interpretations. Recently, M. B. Knickelbein and coworkers (Ref. 16) have confirmed the long standing supposition that $O_2(^1\Sigma)$ is quenched to $O_2(^1\Delta)$. This result is included in Table 1. Since k_3 is spin-allowed and k_2 is not, the assumption is made that k_3 and k_1 contribute all of the observed second order removal.

Numerous $O_2(^1\Delta)$ quenching studies have been conducted (Refs. 20--22, 37, 38, 39). The only relevant gas phase rate coefficient for $O_2(^1\Delta)$ that remains unmeasured is for quenching by H_2O_2. The rate coefficient for this process would have to be very large to compete with the other, more abundant quenchers. It is more likely that species such as H_2O_2 and Cl_2 influence the walls and increase the heterogeneous quenching rates. Indeed, better heterogeneous quenching data for surfaces contaminated with basic hydrogen peroxide, HCl or other species is required. Some data on the wall deactivation of singlet oxygen has been reported (Ref. 40).

For the gas phase quenching of $O_2(^1\Sigma)$, all the relevant rate coefficients have been reliably measured (Refs. 15, 17, 20, 41) except for chlorine and hydrogen peroxide which have been qualitatively measured or estimated. Wall losses may or may not be important depending on the density of the quenchers and flow geometry. The $O_2(^1\Sigma)$ is in steady state, as given by the pooling reaction and quenching reactions.

The analytic solution for the total decay of $O_2(^1\Delta)$, assuming that $O_2(^1\Sigma)$ is in steady state, may be written:

$$[O_2(^1\Delta)]^{-1} = \{ ([O_2(^1\Delta)]_{t=0})^{-1} + A/B \} \exp(Bt) - A/B \qquad (1)$$

where

$$A = k_1 + k_2 + 2 k_3$$

$$B = k_{20} + k_{14}[O_2(^3\Sigma)] + k_{15}[H_2O] + k_{16}[Cl_2] + k_{17}[H_2O_2] + k_{18}[He]$$

The traditional "chi-curve" analysis (Ref. 42) for the transport of singlet oxygen in COIL devices is based on this solution.

There is a general lack of temperature dependent quenching data for singlet oxygen. Given that all measured activation energies are small and that temperature rise in noncatalytic ducts should be small, the lack of $k(T)$ data is not a primary problem in this region.

3.2 IODINE DISSOCIATION

Despite the work done on the I_2 dissociation mechanism since the original papers of R. G. Derwent and B. A. Thrush (Refs. 12, 43, 44), much of the knowledge is empirical and descriptive at best. Originally, the dissociation mechanism was postulated to occur primarily through $O_2(^1\Sigma) + I_2$ (Ref. 12). However, the dissociation in COIL devices, where significant water concentrations severely reduce the steady-state singlet sigma oxygen concentrations, is too fast and efficient to be attributed solely to this mechanism (Refs. 17, 24). Multistep dissociation mechanisms involving $O_2(^1\Delta)$ were then investigated. S. J. Arnold originally postulated a sequence of two or more $O_2(^1\Delta)$ and $I_2(X)$ collisions as a source of atomic iodine (Ref. 45). Such a mechanism requires an intermediate I_2 state to store the energy between $O_2(^1\Delta)$ collisions. An energy level diagram for oxygen and iodine is shown in Fig. 1.

The spectroscopic studies by J. Tellinghuisen (Ref. 46) demonstrated that $I_2(A')$ is not energetically accessible from one $O_2(^1\Delta)$ collision. However, vibrationally excited ground state iodine, I_2^*, is produced in collisions with excited oxygen and excited iodine atoms (Refs. 7, 25, 47). The kinetics of I_2^* have been studied in flow tube reactors (Refs. 25, 27) and a model formulated for the dissociation of I_2 based on this vibrational intermediate (Ref. 27). A sample of the typical flow tube data is shown in Fig. 3.

All studies have shown that the rate of iodine dissociation accelerates as the dissociation proceeds. Evidence is strong that the first step in the sequential excitation and dissociation of I_2 is given by $I^* + I_2 \longrightarrow I + I_2^*$.
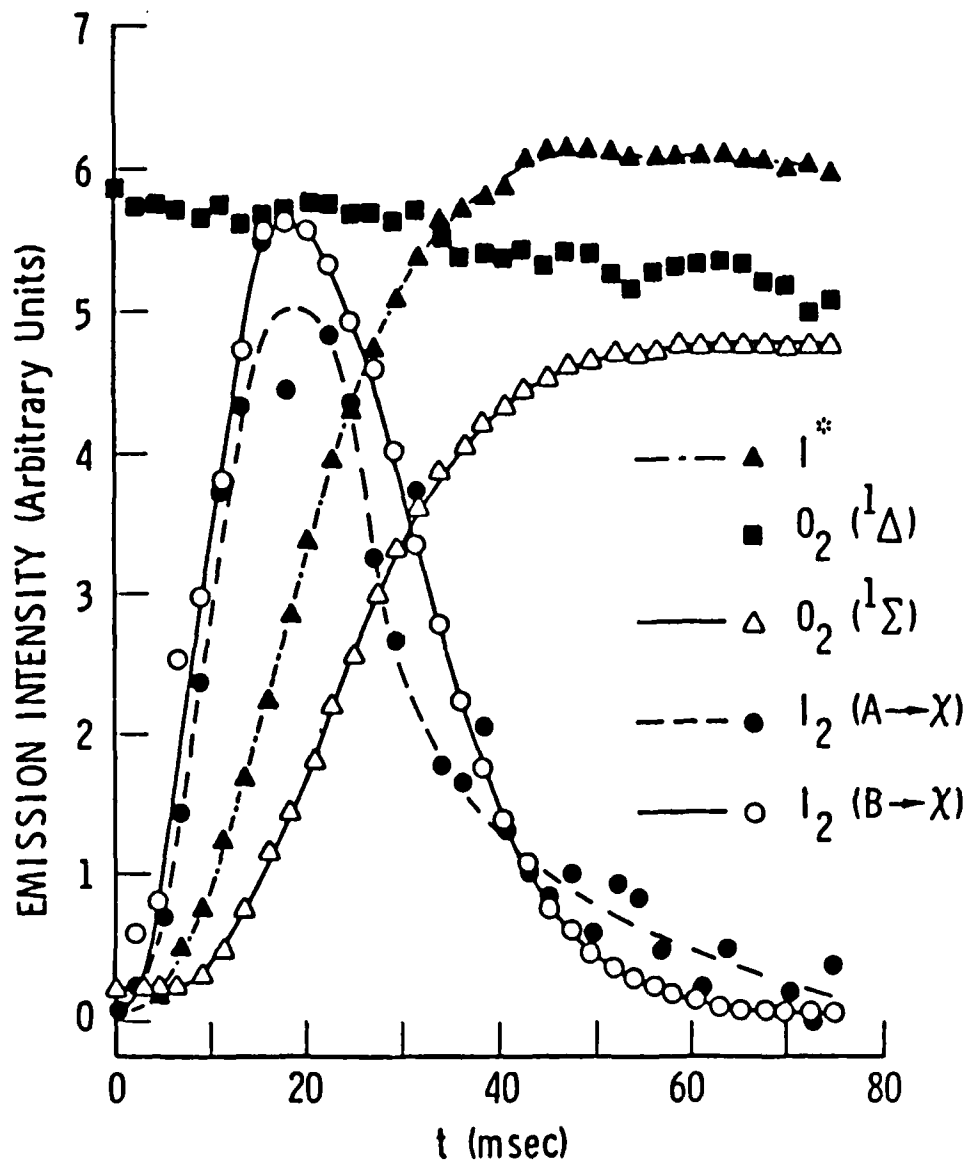
Figure 3. Time profiles of important species in the dissociation of molecular iodine by singlet oxygen under flow tube conditions. This figure is reproduced from Ref. 27.

The dissociation is then completed by $I_2{}^* + O_2({}^1\Delta) \longrightarrow 2I + O_2({}^3\Sigma)$. The excited iodine atoms, $I^* = I({}^2P_{1/2})$, needed for process (32) are formed from process (40) and require an initiation step, probably given by process (21) or (32) of Table 2. Research groups (Refs. 7, 25, and 47), have observed high vibrational levels of $I_2{}^*$ from I^* and $O_2({}^1\Delta)$ collisions with I_2 directly or in a COIL environment. Recently, (Ref. 48) experimenters attempted a state-to-state model which competed $I_2(X)$ vibrational relaxation against its dissociation by $O_2({}^1\Delta)$. This competition is reasonable because the first process must occur sequentially in a cascade down a substantial number of quantum levels while the latter can occur in a single step.

Recent work (Ref. 49) has emphasized the idea that excitation into the $I_2(A')$ state, and presumably into the more weakly bound $I_2(A)$ state to which it is collisionally coupled, creates a situation where iodine atoms are thermodynamically favored. In addition, the dissociation rates from all the vibrational levels of these electronic states are fast.

H. V. Lilenfeld (Ref. 25) has postulated from the observation of $I_2(A-X)$ emission scaling that dissociation of $I_2(A)$ can occur either through the expenditure of an $O_2({}^1\Delta)$ or through a collision with the buffer gas. The later processes have substantial activation energies except for I_2 as the collision partner (Ref. 50). J. Tellinghuisen has postulated that the process $I_2(A') + I_2 \longrightarrow I_3 + I$ is responsible (Ref. 50). The rate coefficient for this process is so large that it could be much more important than process (25) in the COIL mixing zones.

In summary, the dissociation of molecular iodine in the presence of singlet oxygen is slowly initiated by process (32) followed by process (34) or by process (21) directly. Initially formed iodine atoms are rapidly excited from process (40) and the dissociation accelerates as process (33) begins to dominate the slower process (32).

The iodine dissociation mechanism as described in Table 2 is an empirical description of the way I_2 dissociates in flow tube studies where the reagents are essentially premixed and the excited state densities are low. The order of the dissociation process is known with modest accuracy. The mechanism is

not well known and inferred from the reaction order. The efficiency of this dissociation process is perhaps more uncertain than its rate. One of the most critical issues facing COIL modeling is the description of the number of $O_2(^1\Delta)$ required to dissociate an I_2 and where the residual energy is deposited in the flow.

3.3 LASER CAVITY KINETICS

The most important processes in the fully dissociated iodine regime are processes (40-41), the pump and inverse reactions. It should be noted that k_{41} has been measured while k_{40} has been calculated from the equilibrium constant. H. V. Lilenfeld has confirmed the value of the equilibrium constant, $k_{40}/k_{41} =$ 0.75 exp(-403/T), by measuring all four species (Ref. 10). The data are not highly precise, however.

Three major processes can remove energy from the coupled I^* and $O_2(^1\Delta)$ system: (1) pooling, (2) water quenching, and (3) stimulated emission. A simple model for the extraction of lasing photons from this chemical system has been developed (Ref. 51).

The loss of energy from the highly coupled equilibrium states is measured by watching the decay of the I^* - $O_2(^1\Delta)$ system. One such loss is second order, namely the collisions between I^* and $O_2(^1\Delta)$. The energy pooling to form $O_2(^1\Sigma)$ is not the only product channel; quenching of either or both reactants is possible. As with the pure singlet oxygen pooling rate, the branching among product channels is not well described. The nonpooling contribution is arbitrarily assigned to process (45).

The quenching of $I(^2P_{1/2})$ has been studied for many years and most relevant removal rates are known (Refs. 30--33, 35, & 37). I^* quenching by water can have a substantial effect on device performance. The recommended value given for this rate coefficient in Table 3 was obtained in an experiment by A. J. Grimley and P. L. Houston (Ref. 30). The quenching rate for I^* by chlorine has been consistently overestimated, since the secondary products ICl and Cl atoms also quench I^*. The current recommended rate coefficient is

consistent with work of H. V. Lilenfeld (Ref. 25) who derived $k_{54} + k_{55} = 5.5 \pm 0.8 \times 10^{-15}$ cm^3/molecule-s. The rate coefficients for these chlorine reactions are sufficiently slow that they may be ignored in system modeling.

3.4 THE KINETIC DATA BASE

Although the current data base given in Tables 1--4 includes approximately 60 processes, many more reactions could be included. This is particularly true if individual vibrational states of iodine and oxygen were included. The current data base is not intended to be complete, but rather to provide the basis for a relatively simple standard rate package.

A numbering scheme for the reaction data base has been implied in Tables 1--4. This numbering scheme has been developed to segment the model into logical blocks that can be used in an identical manner by different modelers.

4.0 THE STANDARD CHEMICAL OXYGEN-IODINE LASER KINETICS PACKAGE

The current AFWL Standard Chemical Oxygen-Iodine Laser Kinetics Package is given in Table 5. All rate coefficients are reported at T = 295 ± 5 K.

The results of a detailed rate coefficient sensitivity analysis (Ref. 52) indicate that a reduced set of reactions adequately represents the essential features of COIL gas phase kinetics. Two reduced packages developed from this sensitivity analysis are presented in Tables 6--8. These reduced rate packages may be discussed with AFWL, and may prove useful for economical operation of test calculations on expensive codes incorporating mixing and optics. It should be noted that these smaller rate packages deviate from the data base in that the second order removal of $O_2(^1\Delta)$ is handled differently. In order to reduce the number of reactions, the deactivation of $O_2(^1\Sigma)$ is chosen so that the product is $O_2(^3\Sigma)$ and processes (2-3) are eliminated.

While no attempt to include temperature dependent rate coefficients was made in the current standard package, some experimental data for the more important temperature dependent rate coefficients is provided in Table 8.

TABLE 5. Standard AFWL rate package (T = 295 $\pm$ 5 K).

Kinetic Process	Recommended Rate Coefficient (cm^3/molecule-s)
$O_2(^1\Delta) + O_2(^1\Delta) \longrightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$	2.7×10^{-17}
$O_2(^1\Delta) + O_2(^1\Delta) \longrightarrow O_2(^1\Delta) + O_2(^3\Sigma)$	0
$O_2(^1\Delta) + O_2(^1\Delta) \longrightarrow O_2(^3\Sigma) + O_2(^3\Sigma)$	1.7×10^{-17}
$O_2(^1\Sigma) + O_2(^3\Sigma) \longrightarrow O_2(^1\Delta) + O_2(^3\Sigma)$	3.9×10^{-17}
$O_2(^1\Sigma) + H_2O \longrightarrow O_2(^1\Delta) + H_2C$	6.7×10^{-12}
$O_2(^1\Sigma) + Cl_2 \longrightarrow O_2(^1\Delta) + Cl_2$	2.0×10^{-15}
$O_2(^1\Sigma) + H_2O_2 \longrightarrow O_2(^1\Delta) + H_2O_2$	3.3×10^{-13}
$O_2(^1\Sigma) + He \longrightarrow O_2(^1\Delta) + He$	1.0×10^{-17}
$O_2(^1\Delta) + O_2(^3\Sigma) \longrightarrow O_2(^3\Sigma) + O_2(^3\Sigma)$	1.6×10^{-18}
$O_2(^1\Delta) + H_2O \longrightarrow O_2(^3\Sigma) + H_2O$	4.0×10^{-18}
$O_2(^1\Delta) + Cl_2 \longrightarrow O_2(^3\Sigma) + Cl_2$	6.0×10^{-18}
$O_2(^1\Delta) + H_2O_2 \longrightarrow O_2(^3\Sigma) + H_2O_2$	0
$O_2(^1\Delta) + He \longrightarrow O_2(^3\Sigma) + He$	8.0×10^{-21}
$I_2(X) + O_2(^1\Sigma) \longrightarrow I + I + O_2(^3\Sigma)$	4.0×10^{-12}
$I_2(X) + O_2(^1\Sigma) \longrightarrow I_2(X) + O_2(^1\Delta)$	0
$I_2(X) + O_2(^1\Sigma) \longrightarrow I_2(X) + O_2(^3\Sigma)$	0
$I_2(X) + O_2(^1\Sigma) \longrightarrow I_2(A,A') + O_2(^3\Sigma)$	1.6×10^{-11}
$I_2(A,A') + O_2(^1\Delta) \longrightarrow I + I + O_2(^3\Sigma)$	1.0×10^{-11}
$I_2(A,A') + O_2(^1\Delta) \longrightarrow I_2(B) + O_2(^3\Sigma)$	8.0×10^{-11}
$I_2(B) \longrightarrow I_2(X) + h\nu$	$6 \times 10^5 \ sec^{-1}$
$I_2(B) \longrightarrow I + I$	$6 \times 10^5 \ sec^{-1}$
$I_2(X) + O_2(^1\Delta) \longrightarrow I_2^\bullet + O_2(^3\Sigma)$	7.0×10^{-15}
$I_2(X) + I^\bullet \longrightarrow I_2^\bullet + I$	3.8×10^{-11}
$I_2(X) + I^\bullet \longrightarrow I_2(X) + I$	0
$I_2^\bullet + O_2(^1\Delta) \longrightarrow I + I + O_2(^3\Sigma)$	3.0×10^{-10}
$I_2^\bullet + O_2(^3\Sigma) \longrightarrow I_2(X) + O_2(^3\Sigma)$	5.0×10^{-11}
$I_2^\bullet + H_2O \longrightarrow I_2(X) + H_2O$	3.0×10^{-10}
$I_2^\bullet + He \longrightarrow I_2(X) + He$	4.0×10^{-12}
$I_2^\bullet \longrightarrow I_2(X)$	0
$I_2^\bullet + I^\bullet \longrightarrow I + I + I$	0
$I + O_2(^1\Delta) \longrightarrow I^\bullet + O_2(^3\Sigma)$	7.8×10^{-11}

TABLE 5. (Concluded).

I^*	$+ O_2(^3\Sigma)$	$\rightarrow$ I	$+ O_2(^1\Delta)$	2.7×10^{-11}
I	$+ O_2(^1\Delta)$	$\rightarrow$ I	$+ O_2(^3\Sigma)$	1.0×10^{-15}
I^*	$+ O_2(^3\Sigma)$	$\rightarrow$ I	$+ O_2(^3\Sigma)$	0
I^*	$+ O_2(^1\Delta)$	$\rightarrow$ I	$+ O_2(^1\Sigma)$	1.1×10^{-13}
I^*	$+ O_2(^1\Delta)$	$\rightarrow$ I	$+ O_2(^1\Delta)$	1.1×10^{-13}
I^*	$+ O_2(^1\Delta)$	$\rightarrow$ I	$+ O_2(^3\Sigma)$	0
I^*	$+ I$	$\rightarrow$ I	$+ I$	1.6×10^{-14}
I^*	$+ H_2O$	$\rightarrow$ I	$+ H_2O$	2.0×10^{-12}
I^*	$+ H_2O_2$	$\rightarrow$ I	$+ H_2O_2$	2.5×10^{-11}

19

TABLE 6. Reduced AFWL rate package (Mod. 1)

Kinetic Process	Recommended Rate Coefficient (cm^3/molecule-s)
$O_2(^1\Delta) + O_2(^1\Delta) \longrightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$	2.7×10^{-17}
$O_2(^1\Sigma) + H_2O \longrightarrow O_2(^3\Sigma) + H_2O$	6.7×10^{-12}*
$O_2(^1\Delta) + O_2(^3\Sigma) \longrightarrow O_2(^3\Sigma) + O_2(^3\Sigma)$	1.6×10^{-18}
$O_2(^1\Delta) + H_2O \longrightarrow O_2(^3\Sigma) + H_2O$	4.0×10^{-18}
$O_2(^1\Delta) + Cl_2 \longrightarrow O_2(^3\Sigma) + Cl_2$	6.0×10^{-18}
$O_2(^1\Delta) + He \longrightarrow O_2(^3\Sigma) + He$	8.0×10^{-21}
$I_2(X) + O_2(^1\Sigma) \longrightarrow I + I + O_2(^3\Sigma)$	4.0×10^{-12}
$I_2(X) + O_2(^1\Sigma) \longrightarrow I_2(X) + O_2(^1\Delta)$	1.6×10^{-11}
$I_2(X) + O_2(^1\Delta) \longrightarrow I_2^* + O_2(^3\Sigma)$	7.0×10^{-15}
$I_2(X) + I^* \longrightarrow I_2^* + I$	3.8×10^{-11}
$I_2^* + O_2(^1\Delta) \longrightarrow I + I + O_2(^3\Sigma)$	3.0×10^{-10}
$I_2^* + O_2(^3\Sigma) \longrightarrow I_2(X) + O_2(^3\Sigma)$	5.0×10^{-11}
$I_2^* + H_2O \longrightarrow I_2(X) + H_2O$	3.0×10^{-10}
$I_2^* + He \longrightarrow I_2(X) + He$	4.0×10^{-12}
$I + O_2(^1\Delta) \longrightarrow I^* + O_2(^3\Sigma)$	7.8×10^{-11}
$I^* + O_2(^3\Sigma) \longrightarrow I + O_2(^1\Delta)$	2.7×10^{-11}
$I + O_2(^1\Delta) \longrightarrow I + O_2(^3\Sigma)$	1.0×10^{-15}
$I^* + O_2(^1\Delta) \longrightarrow I + O_2(^1\Sigma)$	1.1×10^{-13}
$I^* + O_2(^1\Delta) \longrightarrow I + O_2(^1\Delta)$	1.1×10^{-13}
$I^* + I \longrightarrow I + I$	1.6×10^{-14}
$I^* + H_2O \longrightarrow I + H_2O$	2.0×10^{-12}

*In order to reduce the size of the model, Processes (2) and (3) of Table 5 have been eliminated. In order to correctly mimic the observed kinetics, the artificial assumption of quenching $O_2(^1\Sigma)$ to $O_2(^3\Sigma)$ by Process (2) above is introduced.

TABLE 7. Reduced AFWL rate package (Mod. 2)

Kinetic Process					Recommended Rate Coefficient $(cm^3/molecule\text{-}s)$
$O_2(^1\Delta)$ + $O_2(^1\Delta)$	-->	$O_2(^1\Sigma)$	+	$O_2(^3\Sigma)$	2.7×10^{-17}
$O_2(^1\Sigma)$ + H_2O	-->	$O_2(^3\Sigma)$	+	H_2O	6.7×10^{-12}*
$I_2(X)$ + $O_2(^1\Sigma)$	-->	I	+	I + $O_2(^3\Sigma)$	4.0×10^{-12}
$I_2(X)$ + $O_2(^1\Delta)$	-->	I_2^*	+	$O_2(^3\Sigma)$	7.0×10^{-15}
$I_2(X)$ + I^*	-->	I_2^*	+	I	3.8×10^{-11}
I_2^* + $O_2(^1\Delta)$	-->	I	+	I + $O_2(^3\Sigma)$	3.0×10^{-10}
I_2^* + H_2O	-->	$I_2(X)$	+	H_2O	3.0×10^{-10}
I + $O_2(^1\Delta)$	-->	I^*	+	$O_2(^3\Sigma)$	7.8×10^{-11}
I^* + $O_2(^3\Sigma)$	-->	I	+	$O_2(^1\Delta)$	2.7×10^{-11}
I^* + $O_2(^1\Delta)$	-->	I	+	$O_2(^1\Sigma)$	1.1×10^{-13}
I^* + H_2O	-->	I	+	H_2O	2.0×10^{-12}

*In order to reduce the size of the model, Processes (2) and (3) of Table 5 have been eliminated. In order to correctly mimic the observed kinetics, the artificial assumption of quenching $O_2(^1\Sigma)$ to $O_2(^3\Sigma)$ by Process (2) above is introduced.

TABLE 8. Reduced AFWL rate package (Mod. 2) available
temperature dependent rate data.

Kinetic Process	Recommended Rate Coefficient (cm^3/molecule-s)
$O_2(^1\Delta) + O_2(^1\Delta) \longrightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$ (Heidner et al [26]; Lilenfeld [9])	$9.5 \times 10^{-28}T^{3.8}\exp(700/T)$
$O_2(^1\Sigma) + H_2O \longrightarrow O_2(^3\Sigma) + H_2O$ (no measurement reported)	6.7×10^{-12}
$I_2(X) + O_2(^1\Sigma) \longrightarrow I + I + O_2(^3\Sigma)$ (no measurement reported)	4.0×10^{-12}
$I_2(X) + O_2(^1\Delta) \longrightarrow I_2^* + O_2(^3\Sigma)$ (no measurement reported)	7.0×10^{-15}
$I_2(X) + I^* \longrightarrow I_2^* + I$ (Deakin and Husain [35], normalized to Grimley and Houston [23])	$1.4 \times 10^{-13}\exp(1660/T)$
$I_2^* + O_2(^1\Delta) \longrightarrow I + I + O_2(^3\Sigma)$ (no measurement reported)	3.0×10^{-10}
$I_2^* + H_2O \longrightarrow I_2(X) + H_2O$ (no measurement reported)	3.0×10^{-10}
$I + O_2(^1\Delta) \longrightarrow I^* + O_2(^3\Sigma)$ (calculated from 9 by microscopic reversibility)	$2.33 \times 10^{-8}T^{-1}$
$I^* + O_2(^3\Sigma) \longrightarrow I + O_2(^1\Delta)$ (Deakin and Husain [35], normalized to Young and Houston [24])	$3.1 \times 10^{-8}T^{-1}\exp(-403/T)$
$I^* + O_2(^1\Delta) \longrightarrow I + O_2(^1\Sigma)$ (Heidner et al [26]; Lilenfeld [9])	$4.0 \times 10^{-24}T^{3.8}\exp(700/T)$
$I^* + H_2O \longrightarrow I + H_2O$ (no measurement reported)	2.0×10^{-12}

5.0 CONCLUSIONS AND RECOMMENDATIONS

A standardized rate package for modeling the gas phase kinetics of chemical oxygen-iodine lasers has been developed to provide a basis for comparing the results of various research groups and to provide for optimal information exchange. By reviewing the kinetic data base, several prominent problem areas in fully understanding COIL kinetics have been identified.

Kinetics in the generator duct are fairly well understood. A more accurate rate for the total second order loss of $O_2(1\Delta)$, wall deactivation coefficients for $O_2(^1\Delta)$, and the energy disposal in $O_2(^1\Sigma)$ quenching are important areas for further study. The mechanism for the dissociation of molecular iodine by singlet oxygen is poorly understood. Areas of particular interest in this dissociation process include: (1) quantitative identification of intermediates, (2) the average number of $O_2(^1\Delta)$ required to dissociate one iodine molecule, and (3) the temperature dependence of the dissociation rate and efficiency. The kinetics after complete iodine dissociation are fairly well characterized, but temperature dependent rate coefficients are needed. A test of the current rate package under supersonic COIL device conditions has not been completed. Such a program should be conducted with extensive diagnostics to characterize all the important chemical species, including excited molecular iodine states involved in dissociation.

AFWL encourages active discussion and investigation into the many complex issues associated with the modeling of chemical oxygen-iodine lasers. It is hoped that this AFWL Standard Chemical Oxygen-Iodine Laser Kinetics Package will serve as a good basis for future work in this area.

REFERENCES

1. L. G. Vinogradova, M.V. Zagidullin, V.I. Igoshin, V.A. Katulin, and N.L. Kupriyanov, "Analysis of the Energetics of a Chemical Oxygen-Iodine Laser", Sov J Quantum Electron, 12(6), 752, 1982.

2. A.I. Didyukov, Yu.I. Krasnoshchekov, Yu.A. Kulagin, V.A. Morozov, S.A. Reshetnyak, and L.A. Shelepin, "Kinetics of Physical Processes in an Oxygen-Iodine Medium", Sov J Quantum Electron, 12(4), 399, 1982.

3. M.V. Zagidullin, V.I. Igoshin, V.A. Katulin, and N.L. Kupriyanov, "Numerical Modeling of a Chemical Oxygen-Iodine Laser", Sov J Quantum Electron, 12(9), 1235, 1982.

4. N.G. Basov, M.V. Zagidullin, V.I. Igoshin, V.A. Katulin, and N.L. Kupriyanov, "Active Medium of Chemical Oxygen-Iodine Laser", Sov J Quantum Electron, 16(4), 510, 1986.

5. R.F. Shea, Memorandum for Record on COIL Kinetic Rate Package, Air Force Weapons Laboratory, AFWL/ARAY, Kirtland Air Force Base, New Mexico 87117-6008, 16 Nov 1982.

6. W.E. McDermott, N.R. Pchelkin, D.J. Benard, R.R. Bousek, "An Electronic Transition Chemical Laser", Appl Phys Lett, 32, 469, 1978.

7. M.H. Van Benthem and S.J. Davis, "Detection of Vibrationally Excited I_2 in the Iodine Dissociation Region of Chemical Oxygen-Iodine Lasers", J Phys Chem, 87, 2153, 1983.

8. R.F. Heidner III, "Behavior of Singlet Oxygen in the Oxygen-Iodine Transfer Laser", J Photochem, 25, 449, 1984.

9. R.M. Badger, A.C. Wright, and R.F. Whitlock, "Absolute Intensities of the Discrete and Continuous Absorption Bands of Oxygen Gas at 1.26 and 1.065 μm and the Radiative Lifetime of the Singlet-Delta State of Oxygen", J Chem Phys, 43, 4345, 1965.

10. H.V. Lilenfeld, Oxygen-Iodine Laser Kinetics, AFWL-TR-83-01, 1983.

11. G.A. Fisk and G.N. Hays, "Kinetic Rates in the Oxygen-Iodine System", J Chem Phys, 77, 4965, 1982.

12. R.G. Derwent and B.A. Thrush, "Excitation of Iodine by Singlet Molecular Oxygen. Part I. Mechanism of the I_2 Chemiluminescence", J Chem Soc Faraday II, 68, 720, 1972.

13. R.F. Heidner III, C.E. Gardner, T.M. El-Sayad, G.I. Segal, and J.V.V. Kasper, "Temperature Dependence of the $O_2(1\Delta)$ + $O_2(1\Delta)$ and $I(2P_{1/2})$ + $O_2(1\Delta)$ Energy Pooling", J Chem Phys, 74, 5618, 1981.

14. R.F. Heidner III, "Critical Summary of Gas Phase and Heterogeneous Deactivation of $O_2(1\Delta,1\Sigma)$ in COIL Devices", Private Communication, 1987.

15. S. A. Lawton, S.E. Novick, H.P. Broida, and A.V. Phelps, "Quenching of Optically Pumped $O_2(b1\Sigma g)$ by Ground State O_2 Molecules", <u>J Chem Phys</u>, <u>66</u>, 1381, 1977.

16. M.B. Knickelbein, K.L. Marsh, O.E. Ulrich, and G.E. Busch, "Energy Transfer Kinetics of Singlet Molecular Oxygen: The Deactivation Channel for $O_2(b1\Sigma g)$", <u>J Chem Phys, 87</u>, 2392, 1987.

17. R.G. Aviles, D.F. Muller and P.L. Houston, "Quenching of $O_2(b1\Sigma)$ by CO_2, H_2O, I_2", <u>Appl Phys Lett, 37</u>, 358, 1980.

18. A.T. Pritt, Jr, private communication to R.F. Heidner, 1979.

19. R.F. Heidner, unpublished (1982). Based on Kear-Abrahmson E-V Model (see <u>J Photocehm, 3</u>, 409, 1974.

20. K.H. Becker, W Groth and U Schurath, "The Quenching of Metastable O (alΔ) and $O_2(1\Sigma g)$ Molecules", <u>Chem Phys Lett, 8</u>, 259, 1971.

21. P. Borrell, P.M. Borrell, and M.D. Pedley, "Deactivation of Molecular Oxygen, $O_2(al\Delta g)$, by Oxygen", <u>Chem Phys Lett, 51</u>, 300, 1977.

22. J.P. Singh, J. Bachar, D.W. Setser, S Rosenwaks, "Electronic to Vibrational Energy Transfer Studies of Singlet Molecular Oxygen. 1. $O_2(al\Delta)$", <u>J Phys Chem, 89</u>, 5347, 1985.

23. R.J. Collins, D. Husain, and R.J. Donovan, "Kinetic and Spectroscopic Studies of $O_2(al\Delta g)$ by Time-Resolved Absorption Spectroscopy in the Vacumm Unltraviolet", <u>J Chem Soc Faraday II, 69</u>, 145, 1973.

24. D.F. Muller, R.H. Young, P.L. Houston, and J.R. Wiesenfeld, "Direct Observation of I_2 Collisional Dissociation by $O_2(b1\Sigma g)$", <u>Appl Phys Lett</u>, <u>38</u>, 404, 1981.

25. H.V. Lilenfeld, G.R. Bradburn, and F.E. Hovis, <u>Oxygen-Iodine Laser Kinetics</u>, AFWL-TR-84-151, Air Force Weapons Laboratory, Kirtland AFB, N. Mex. 1985.

26. G.A. Capalle and H.P. Broida, "Lifetimes and Quenching Cross Sections of $I_2(B)$", <u>J Chem Phys, 58</u>, 4212, 1973.

27. R.F. Heidner III, C.E. Gardner, G.I. Segal, and T.M. El-Sayad, "Chain Reaction Mechanism for I_2 Dissociation in the $O_2(1\Delta)$ - I Atom Laser", <u>J Phys Chem, 87</u>, 2348, 1983.

28. A.J. Grimley and P.L. Houston, "Electronic-to-Vibrational Energy Transfer from $I(2P_{1/2})$. I. HCl, HBr, and NO," <u>J Chem Phys, 68</u>, 3366, 1978.

29. A.T. Young and P.L. Houston, "The $I(2P_{1/2}) + O_2 <--> I(2P_{3/2}) + O_2(1\Delta)$ Equilibrium", <u>J Chem Phys, 78</u>, 2317, 1983.

30. A.J. Grimley and P.L. Houston, "Electronic-to-Vibrational Energy Transfer from $I(2P_{1/2})$. II. H_2O, HDO, and D_2O", <u>J Chem Phys, 69</u>, 2339, 1978.

31. D.H. Burde and R.A. McFarlane, "Collisional Quenching of Excited Iodine Atoms by Selected Molecules", J Chem Phys, 64, 1850, 1976.

32. J.R. McDonald and J.K. Hancock, "I Atom Bimolecular Quenching by O_2, H_2O, H_2O_2, and H_2", Memo Report 3395, NRL, Washington, DC, 1976.

33. R.J. Donovan and D. Husain, "Electronically Excited Iodine Atoms. Part 2", Trans Far Soc, 62, 1050, 1966.

34. G. Brederlow, E. Fill, and K.J. Witte, The High-Power Iodine Laser, Springer in Optical Sciences, Vol 34, 1983.

35. G.E. Hall, S. Arepalli, P.L. Houston and J.R. Weisenfeld, "Collisional Quenching of Excited Iodine Atoms ($2P_{1/2}$) by Cl_2 in a Flow System", J Chem Phys, 82, 2590, 1985.

36. M.A.A. Clyne and H.W. Cruse, "Atomic Resonance Fluorescence Spectrometry for the Rate Constants of rapid Bimolecular Reactions", J Chem Soc Faraday II, 68, 1377, 1972.

37. J.J. Deakin and D Husain, "Temperature Dependence of Collisionally Induced Spin Orbit Relaxation of Electronically Excited Iodine Atoms $I(2P_{1/2})$", J Chem Soc Faraday II, 68, 1603, 1972.

38. F.D. Findlay and D.R. Snelling, "Collisional Deactivation of $O_2(1\Delta g)$", J Chem Phys, 55, 545, 1971.

39. R.G.O. Thomas and B.A. Thrush, "Quenching of $O_2(1\Delta g)$ by Ground State O_2," JCS Faraday II, 71, 664, 1975.

40. T.G. Slanger, Surface Generation of Electronically Excited States of O_2, AFOSR-TR-86-0849, Air Force Office of Scientific Research, Bolling AFB, DC, 1986.

41. L.R. Martin, R.B. Cohen, and J.I. Schatz, "Quenching of Laser Induced Fluoresence of $O_2(b1\Sigma g)$ by O_2 and N_2", Chem Phys Lett, 41, 394, 1976.

42. J.O. Berg, et al, Oxygen-Iodine Supersonic Technology, AFWL-TR-85-43, Vol 1, Part 1, Air Force Weapons Laboratory, Kirtland AFB, N. Mex., Nov. 1985.

43. J.G. Derwent and B.A. Thrush, "Excitation of iodine by Singlet Molecular Oxygen. Part 2. Kinetics of the Excitation of Iodine Atoms", Disc Faraday Soc, 53, 162, 1972.

44. R.G. Derwent and B.A. Thrush, "The Radiative Lifetime of the Metastable Iodine Atom $I(2P_{1/2})$", Chem Phys Lett, 9, 591, 1971.

45. S.J. Arnold, N Finlayson, and E.A. Ogryzlo, "Some Novel Energy-Pooling Processes Involving $O_2(^1\Delta_e)$," J Chem Phys, 44, 2529, 1966.

46. J. Tellinghuisen, "The D' to A' Transition in I_2," J Mol Spec, 94, 231, 1982.

47. G.E. Hall, W.J. Marinelli, and P.L. Houston, "Electronic-to-Vibrational Energy Transfer from $I(2P_{1/2})$ to I_2 (25 < v < 43)", <u>J Phys Chem. 87</u>, 2153, 1983.

48. D. David, V. Joly, and A. Fausse in "Gas Flow and Chemical Lasers", Proceedings of the 6th International Symposium, S Rosenwaks Ed., Springer Proceedings in Physics 15, Springer - Verlag, Berlin, 1986.

49. J. Tellinghuisen, A.R. Whyte, and L.F. Phillips, "Kinetics of I_2 Following ArF Laser Excitation: Thermal Dissociation of the $Al(2\mu)$ State", <u>J Phys Chem. 88</u>, 6084, 1984.

50. J. Tellinghuisen and L.F. Phillips, "Kinetics of I_2 Following Photolysis at 1930 A: Temperature Dependence of A'-State Quenching", <u>J Phys Chem. 90</u>, 5108, 1986.

51. G.D. Hager and R.H. Humphreys, Jr, <u>A Simple. Analytical Model for Gain Saturation and Power Extraction in the Chemical Oxygen Iodine Laser</u>, AFWL-TR-86-117, Air Force Weapons Laboratory, Kirtland AFB, N. Mex., Oct. 1987.

52. R. Crannage and G.P. Perram, "Kinetic Modeling of Chemical Oxygen-Iodine Lasers," Air Force Weapons Laboratory, Kirtland AFB, N. Mex., to be published.